Name:_____   SID: _Key_

Exam #1

Biophysical Chemistry

Chemistry 130A

Spring 2001

Justify all your assumptions!

Show <u>all</u> your calculations!

Make sure all your conclusions are physically reasonable.

Keep track of units and significant digits!

Underline or Box all your final answers!

Exams in pencil won't be regraded.

1. (9 pts) Thermodynamic Functions

(a) Each integral below represents taking a Carnot engine around one complete cycle. State whether or not the integral is equal to zero and why.

1. $\oint \dfrac{dq_{rev}}{T} = \Delta S = \emptyset$ State function, cycle

2. $\oint dw \neq \emptyset$ path variable

3. $\oint \dfrac{dV}{V} = \emptyset$ $\because V_2 = V_1$ $\therefore \displaystyle\int_{V_1}^{V_2} \dfrac{dV}{V} = \ln \dfrac{V_2}{V_1} = \ln 1 = \emptyset$
   STATE VAR.

4. $\oint (dq + dw) = \Delta E = \emptyset$ STATE FUNCTION

5. $\oint dq \neq \emptyset$ path

1 POINT EACH

(b) Which of the following are state functions and why?

1. **PVT**   STATE FUNCTION ∵ PRODUCT OF STATE VARIABLES IS A STATE FUNCTION

2. **w/q**   NOT STATE FUNCTION ∵ BOTH w & q are PATH VARIABLES SO THEIR QUOTIENT IS A PATH FUNCTION

3. **q + w + PV** $= E + PV = H$ WHICH IS A STATE FUNCTION

4. **E-TS** $= A$; DIFFERENCE BETWEEN TWO STATE FUNCTIONS IS A FUNCTION.

1 POINT EACH

2. (12 pts) Antidepressants and paths.

A pharmacist is considering the use of LiBr to treat manic-depressive patients after reading an advertisement in psychology today that said "Handel wrote The Messiah in seven days. Today he wouldn't have the problem. Lithium."

She is concerned that when solid LiBr is ingested with water, it might release enough heat to make the patient very uncomfortable. She is thinking of the following regimen: **Once Daily: Take 8.7 g of LiBr in 36mls of water**.

From her handy-dandy CRC she pulls out:

LiBr: 87 grams per mole Δ**H** for dissolving LiBr in water: -11.7 kcal/mol

Water: 16 g/mol C_p of LiBr in water is: 0.98 cal/(K g)

She then made the following assumptions: **1)** The LiBr and water mix in the stomach (and LiBr doesn't dissociate) **2)** The reaction occurs so quickly that no heat may leave the stomach (until later) **3)** Everything occurs at 1 atm.

(a) Write down the series of thermodynamic (and chemical) state changes for the process of taking the medication, dissolving of LiBr, and eventual release of heat to the surrounding.

Any indication of : (+2) heat released or dissolution

(+2) sol'n absorbs heat

(+2) sol'n releases heat to surroundings

this includes using formulas rep. these steps in variable form, and descriptions after number cruching.

4

(b) What is the **maximum** temperature reached in the stomach of the patient? Do you think this is ok? Show your thought process!

$$\Delta H = \dfrac{q}{v} \qquad +1$$

$$\underbrace{\left(n_{LiBr}\right)\left(-\Delta H_{diss}\right) = m_{sol'n}\, C_p\, \Delta T}_{+4}$$

wrong n and/or m -1

positive ΔH -1

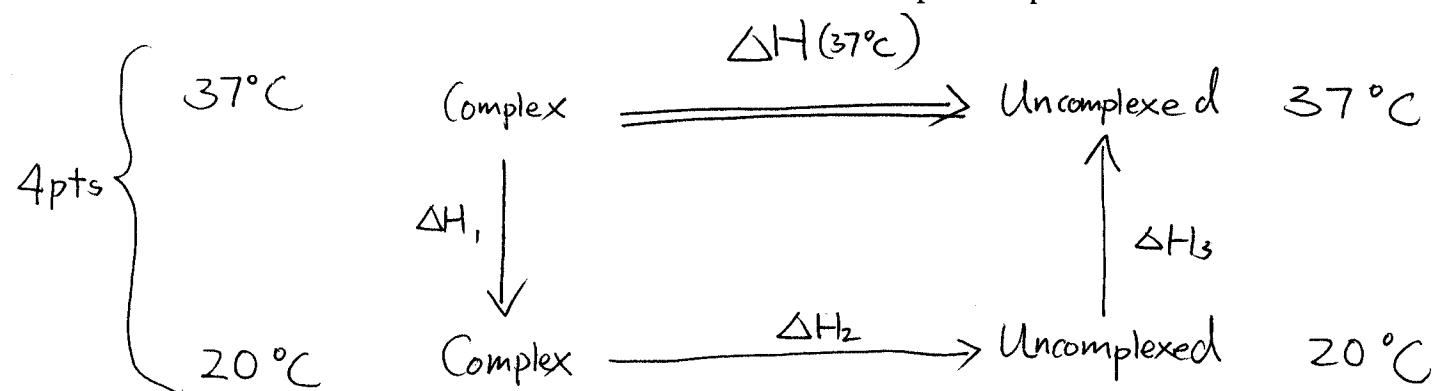arithimetic error $\underline{\quad -1 \quad}$

              $+1$ minimum score

Comment $+1$

3. (12 pts) Chemical Paths

Perhaps the better antidepressant drug, Prozac, blocks the action of the neurotransmitter serotonin by competing for the serotonin binding site. At 20°C, the Prozac-receptor dissociation has an enthalpy of 1200 kJ/mol as measured by titration scanning calorimetry. The molecular weight of the Prozac-receptor complex is 42,000 g/mol

The difference in heat capactity between the complex (Prozac·Receptor) and the free molecules (Prozac+Receptor) has been determined to be $\Delta C_P = C_P^{complexed} - C_P^{uncomplexed} = 1.35$ J/(K gram). Calculate the ΔH per mole of reaction for dissociation of the Prozac-receptor complex at 37°C.

4pts {

37°C   Complex $\xrightarrow{\quad \Delta H(37°C) \quad}$ Uncomplexed 37°C

$\Delta H_1 \downarrow$ $\uparrow \Delta H_3$

20°C   Complex $\xrightarrow{\quad \Delta H_2 \quad}$ Uncomplexed 20°C

}

$$\Delta H(37°C) = \Delta H_1 + \Delta H_2 + \Delta H_3$$

4pts {

$$= C_P^{complexed}(20°C-37°C) + \Delta H(20°C)$$
$$+ C_P^{uncomplexed}(37°C - 20°C)$$

4pts {

$$= \Delta H(20°C) + (20°C-37°C)(C_P^c - C_P^u)$$

$$= \Delta H(20°C) + (-17°C)\Delta C_P$$

" not missing
the sign of ΔC_P
or ΔT "

$$= 1200 \frac{kJ}{mol} + (-17°C)\left[1.35\frac{J}{K·g} · 42000\frac{g}{mol}\right]$$

$$= \underline{\underline{236,1 \frac{kJ}{mol}}}$$

✳ math error: 2pts

6

4. (10 pts) Entropy and other things

(4) (a) Give a formula for the probability that all N molecules of an ideal gas are in one half of a box and not the other. Compare the probability when N equals four to when N is equal to Avagadro's number. What are the implications of this in cells when a protein is present at small numbers (5-10 copies)? (Think, for example, about cell division.)

$$\frac{1}{2^N} \quad or \quad \frac{1}{2^{N-1}} \qquad ; \quad \left(\frac{1}{2}\right)^4 = 0.0625 \qquad ; \quad \left(\frac{1}{2}\right)^{6.02 \times 10^{23}} = 0$$

If a cell contains only a few copies of a protein, there is a significant probably of non-uniform distribution.

(2) (b) The second law of thermodynamics states that any system and its surroundings must continually increase in entropy. However, living organisms constantly create highly ordered structures from less-ordered raw materials. Do living organisms violate the second law? Explain.

Living organisms are not closed systems so the entropy change of the surroundings must be considered. The gain in entropy from the metabolism of nutrients, compensates for the decrease in entropy associated with the growth of the organism.

(4) (c) Do you get more work out of a reversible or irreversible expansion of an ideal gas? Why?

Reversible.

for irreversible expansion $P_{ext} < P_{int}$

for reversible expansion $P_{ext} = P_{int}$; $|dW| = |-P_{ext} dW|$

$|dW_{rev}| > |dW_{irrev}|$

5. (17 pts) Non-ideality

A crazed physicist has made an electron gas in the laboratory. He theorizes, for reasons he doesn't wish to divulge, that the internal energy of this gas is:

$$E(V,T) = (3/2)nRT + X\left(\frac{n}{VT}\right)$$

over some temperature range, with X a positive constant (in units of J*L*K/mol). This second term might describe a repulsive interaction among the electrons in the gas.

The heat capacity of this gas is given by $\quad C_V = \left(\frac{\partial E}{\partial T}\right)_V = (3/2)nR - X\frac{n}{VT^2}$

(a) Recall that $C_V = (3/2)nR$ for an ideal gas. Does the form of C_V above make sense, in light of the fact that our nonideal gas has repulsive interactions? Explain.

YES IT MAKES SENSE. SMALLER HEAT CAPACITY ∴ FEWER TRANSLATIONAL DEGREES OF FREEDOM; IN CONTACT MORE OFTEN.

2 POINTS FOR TRYING
5 POINTS MOSTLY CORRECT
7 POINTS ALL CORRECT

(b) Intuitively, we expect $C_V > 0$ always (because increasing the temperature of a system should increase its energy). Is the C_V above physically reasonable in this sense? Explain.

ACTUALLY, BOTH ANSWERS ARE ACCEPTABLE PROVIDED YOU JUSTIFIED IT IN SOME WAY.

3 PTS FOR JUSTIFIED ANSWERS
0 PTS FOR LEAVING BLANK OR NONSENSE

(c) For an ideal gas, ΔE for an isothermal expansion is 0. Will ΔE for our nonideal gas be greater than, less than, or equal to zero when it undergoes an isothermal expansion?

$V_2 > V_1 \qquad T$ CONSTANT

$-E(V_1,T) = \frac{3}{2}nRT + X\frac{n}{V_1T}$

$+E(V_2,T) = \frac{3}{2}nRT + X\frac{n}{V_2T}$

$\Delta E = \emptyset + \frac{Xn}{T}\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$

SINCE $V_2 > V_1$

$\left(\frac{1}{V_2}-\frac{1}{V_1}\right) < \emptyset$

$\therefore \Delta E < 0$

7 PTS CORRECT ANSWER
5 PTS MOSTLY CORRECT
2 PTS SOME ANSWER